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FINAL REPORT

Researches on Alloys Rapidly Quenched from the Melt

(Office of Naval Research Grant No. N-0014-78-G-0039)

1. Introduction

The original research proposal, dated September 1977, on which the O.N.R. grant to the Rapid Quenching Group at Sussex University was based, incorporated five principal topics:

(a) The martensitic transformation in rapidly quenched samples (morphology, crystallography, mechanical properties);

(b) Investigation on metallic glasses (density, TEM, crystallization);

(c) Transformations in and strength of non-ferrous metastable alloys (age-hardening, grain-size effects);

(d) Rapidly quenched tool steels (hardening, TEM); and

(e) Diffusion in metallic glasses.

We have made significant advances in all of these fields and subfields (except for age-hardening in rapidly quenched alloys), and, under heading (b), went well beyond our original brief in a detailed study of thermal relaxation in glasses.

The range and variety of the observations made is much too great for a detailed account in this summary report: instead, I propose to list the 12 Technical Reports issued during the period of the grant, the names of the participants in the research, and the papers published or in press under each heading. Then I shall very briefly indicate what I regard as our principal findings, and suggest what needs to be done next.

Throughout the period of the research, the work was jointly funded by O.N.R. and the Science Research Council (of the U.K.): the O.N.R. funding paid the salaries of several investigators and of a secretary for all or part of the period, paid for some of the materials used and for much travel, especially to conferences. We are all extremely indebted to O.N.R. for the crucial part played by its finance in making possible this intensively collaborative research programme, and for its willingness to support, in this exceptional manner, a British research group.

It is a matter of great regret that financial stringency has now (July 1981) forced a sharp contraction of the research effort on rapid quenching at Sussex University: but the leaders of that research, Prof. Cahn, Dr. Cantor and Dr. Scott, will each continue in his own place to carry out research in this lively field of science.

2. Technical Reports Issued (omitting End-of-Year Letters)

1. June 1979: R.W. Cahn, B. Cantor, M.G. Scott:- Researches on Alloys Rapidly Quenched from the Melt - First Annual Report. (53 pages)

2. October 1979: R.W. Cahn, J.E. Evetts, J. Patterson, R.E. Somekh, C.K. Jackson:- Direct Measurement by SIMS of Self-Diffusion of Boron in $Fe_{40}Ni_{40}B_{20}$ Glass. (13 pages). (Prof. Cahn's 4 co-authors were at Cambridge & Harwell.)

3. November 1979: S. Banerjee:- Splat-Quenching of Zirconium Alloys, with Special Reference to Martensite and Precipitate Reactions. (58 pages.)

4. January 1980: S.J.B. Charter, D.R. Mooney, R. Cheese and B. Cantor:- Melt-Spinning of Crystalline Alloys. (11 pages.)

5. January 1980: R. Cheese and B. Cantor:- Superplasticity in Splat-Quenched Pb-Sn Eutectic. (24 pages.)

6. February 1980: R.W. Cahn:- Metallic Glasses - a Review of Physical Characteristics. (33 pages.)

7. May 1980: Y.D. Dong, G. Gregan and M.G. Scott:- Formation and Stability of Nickel-Zirconium Glasses. (22 pages.)

8. May 1980: A. Kursumovic and M.G. Scott:- The Use of Young's Modulus to Monitor Relaxation in Metallic Glasses. (10 pages.)

9. June 1980: J.J. Rayment and B. Cantor:- The As-Quenched Microstructure and Tempering Behaviour of Rapidly Solidified Tungsten Steel. (49 pages.)

10. February 1981: A. Kuršumović, R.W. Cahn and M.G. Scott:- Length Changes During the Structural Relaxation of Metallic Glasses. (6 pages.)

11. February 1981: A. Kuršumović, M.G. Scott, E. Girt and R.W. Cahn:- Changes in the Young's Modulus During Structural Relaxation of a Metallic Glass. (6 pages.) (E. Girt is a collaborator in Yugoslavia.)

12. February 1981: M. Kijek, M. Ahmadzadeh, B. Cantor and R.W. Cahn:- Diffusion in Amorphous Alloys. (4 pages.)

3. Individuals Who Participated in the O.N.R. Research Programme at Sussex University, June 1978-June 1981 (omitting short-term visitors).

(a) Senior Investigators:

Prof. R.W. Cahn, Dr. B. Cantor, Dr. M.G. Scott, Prof. K. Hoselitz (part-time, magnetic studies).

(b) Other Postdoctoral Investigators:

Dr. M. Ahmadzadeh, Dr. S. Banerjee, Dr. Y. Inokuti, Dr. F.E. Luborsky, Dr. J.J. Rayment, Dr. B. Toloui, Dr. T. Watanabe, Dr. D. Akhtar.

(c) Predoctoral Investigators:

Y.D. Dong, G. Gregan, A.R. Heath, M. Kijek, A. Kuršumović, N.A. Pratten, M. Thomas.

(d) Technician:

R. Cheese.

(e) Undergraduates:

S.J.B. Charter, D.R. Mooney.

Many of the above-named were members of the research group for only a portion of the 3-year period.

4. Publications, 1978-81

In the list that follows, each paper is referred to one of the 5 research fields listed in the Introduction, or marked as not being connected with any of these:-

(a) The Martensitic Transformation

1. F. Duflos and B. Cantor, "Martensite in Splat-Quenched Iron and Iron-Nickel", Rapidly Quenched Metals III (Met.Soc., London, 1978) Vol.1, p.110.
2. Y. Inokuti, F. Duflos and B. Cantor, "Martensite Morphology in Rapidly Solidificed Pure Iron", in Phase Transformations (Inst. of Metallurgists, 1979) p.IV-17.
3. Y. Inokuti and B. Cantor, "Martensite Morphology in Rapidly Solidified Fe Alloys", Proc. Int. Conf. on Martensitic Transformations, ICOMAT 1979, p.46.
4. S. Banerjee and B. Cantor, "Martensitic Transformations in Splat-Quenched Zirconium Alloys", Proc. Int. Conf. on Martensitic Transformations, ICOMAT 1979, p.46.
5. J.J. Rayment and B. Cantor, "The Microstructure of Rapidly Solidified Iron-Tungsten-Carbon Alloys", Met. Trans. in press.
6. Y. Inokuti and B. Cantor, "Microstructure and Kinetics of Formation of Martensite in Rapidly Solidified Fe-Ni Alloys", submitted to Acta Met.
7. F. Duflos and B. Cantor, "Microstructure and Microhardness of Ferritic and Martensitic Splat-Quenched Pure Iron", submitted to Acta Met.

(b) Investigations on Metallic Glasses

8. M.G. Scott, "The Crystallization Kinetics of Fe-Ni Based Metallic Glasses", J. Mater. Sci. 13 (1978) 281.
9. M.G. Scott, "Thermal Stability and Crystallization of Metallic Glasses", Rapidly Quenched Metals III (Met.Soc., London, 1978), Vol.1, p.198. (Reprinted in Metals Techn. (1980) p.133.)

10. N.A. Pratten and M.G. Scott, "Annealing Effects in Metal-Metal Amorphous Alloys", Rapidly Quenched Metals III (Met.Soc., London, 1978), Vol.1, p.387.

11. N.A. Pratten and M.G. Scott, "Stability of some Metalloid-Free Metallic Glasses", Scripta Met., 12 (1978) 137.

12. M.G. Scott and T. Watanabe, "Crystallization of Some Metallic Glasses", in Phase Transformations (Inst. of Metallurgists, 1979), p. IV-17.

13. R.W. Cahn, "Order and Holes in Metallic Glasses", in Comptes Rendu 21e Colloque de Metallurgie, 'Alliages et Matériaux Amorphes'. (CEN, Saclay, France, 1979) p.137.

14. K. Hoselitz, "Crystallization of Magnetic Fe-Si-B Glasses", Phys. Stat. Sol. (a) 53, (1979) 423.

15. R.W. Cahn, "Metallic Glasses". Contemp. Phys. 21 (1980) 43.

16. M.G. Scott and T. Watanabe, "Crystallization of the Amorphous Alloy $Fe_{40}Ni_{40}P_{14}B_6$" J. Mat. Sci. 15 (1980) 1131.

17. A. Kursumovic and M.G. Scott, "The Use of Young's Modulus to Monitor Relaxation in Metallic Glasses" Appl. Phys. Letters 37 (1980) 620.

18. Y.D. Dong, G. Gregan and M.G. Scott, "Glass Formation and Stability in the Zr-Ni System", J. Non-Cryst. Solids, 43 (1981) 403.

19. M.G. Scott, "Thermal Stability and Crystallization of Metallic Glasses", Proc. Conf. on Amorphous Metallic Materials, in Physics and Applications (Bratislava, Czechoslovakia), 5 (1980) 291.

20. A. Kuršumović, M.G. Scott, E. Girt and R.W. Cahn. "Changes in the Young's Modulus During Structural Relaxation of a Metallic Glass", Scripta Met. 14 (1980) 1303.

21. A. Kuršumović, R.W. Cahn and M.G. Scott, "Length Changes During the Structural Relaxation of Metallic Glasses", Scripta Met. 14, (1980) 1245.

22. I. Vincze, F. van der Woude and M.G. Scott, "Local Structure of Amorphous Zr_3Fe", Solid State Comm., in press.

23. A. Kursumovic and M.G. Scott, "Structural Relaxation of the Metallic Glass $Fe_{40}Ni_{40}B_{20}$", submitted to Acta Met.

24. M.G. Scott, "Crystallization of Metallic Glasses", in Encyclopedia of Materials Science and Engineering, Pergamon Press, in press.

25. M.G. Scott, "Relaxation of Metallic Glasses", Encyclopedia of Materials Science and Engineering, Pergamon Press, in press.

26. M.G. Scott, "Calorimetric Evidence for Short Range Ordering in a Metallic Glass", submitted to Scripta Met.

27. B. Cantor and P. Ramachandrarao, "A Simple Model for Describing the Thermodynamic Properties of Glassy and Supercooled Liquid Alloys in Terms of the Configuration of Dense Random Packed Structures", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

28. M.G. Scott, R.W. Cahn, A. Kursumovic, E. Girt and B. Njuhovic, "Structural Relaxation of the Metallic Glass $Fe_{40}Ni_{40}B_{20}$", Submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

29. M.G. Scott, G. Gregan and Y.D. Dong, "Crystallization of Zirconium-Nickel Glasses", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

30. R.W. Cahn, B. Toloui, D. Akhtar and M. Thomas, "Radiation Damage in Metallic Glasses", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

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31. S.J.B. Charter, D.R. Mooney, R. CHeese and B. Cantor, "Melt-Spinning of Crystalline Alloys", J. Mat. Sci. (1980) 15, 2658.

32. R. Cheese and B. Cantor, "Superplasticity in Splat-Quenched Pb-Sn Eutectic", Mat. Sci. & Eng. 45 (1980) 83.

33. R.W. Cahn, "Rapid Quenching from the Melt", in Encyclopedia of Materials Science and Engineering, Pergamon Press, in press.

34. S. Banerjee and R.W. Cahn, "Formation of the Zr_2Al Phase in a β-Zr-Al Alloy - A Hybrid of Displacive and Replacive Ordering", to be presented at Int.Conf. on Solid-Solid Transformations, Pittsburgh, August 1981; expanded version submitted to Acta Met.

35. S. Banerjee, B. Cantor and R.W. Cahn, "Sequence of Phase Transformations in Zirconium Alloys During Rapid Quenching from the Liquid State", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

(d) Rapidly Quenched Tool Steels

36. J.J. Rayment and B. Cantor, "Splat-Quenching of High-Speed Tool Steels", Metal Science, 12 (1978) 156.

37. J.J. Rayment and B. Cantor, "Splat-Quenched Tungsten Steels", Rapidly Quenched Metal III (Met.Soc. London, 1978), Vol.1, p.

38. J.J. Rayment and B. Cantor, "The Microstructure of Rapidly Solidified Iron-Tungsten-Carbon Alloys", Met. Trans. in press.

(e) Diffusion in Metallic Glasses

39. R.W. Cahn, J.E. Evetts, J. Patterson, R.E. Somekh and C.R. Jackson "Direct Measurement by SIMS of Self-Diffusion of Boron in $Fe_{40}Ni_{40}B_{20}$ Glass", J. Mat. Sci. 15 (1980) 702.

40. M. Kijek, M. Ahmadzadeh, B. Cantor and R.W. Cahn, "Diffusion in Amorphous Alloys", Scripta Met. 14 (1980) 1337.

41. M. Ahmadzadeh and B. Cantor, "Interstitial Structure and Diffusion in DRP Metallic Glasses", J. Non-Cryst. Solids, 43 (1981) 189.

42. M. Kijek, D. Akhtar, B. Cantor and R.W. Cahn, "Diffusion Rates in Metal-Metal Glasses Measured by Ion Accelerator Techniques", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

43. M. Ahmadzadeh and B. Cantor, "A Monte Carlo Invesigation of Interstitial Jumps in the Diffusion of Small Atoms in Dense Random Packed Structures", submitted for presentation at the Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan, August 1981, and published in the Proceedings.

(f) Miscellaneous

44. K. Hoselitz, "Magnetic Properties of Iron-Boron-Silicon Metallic Glasses", J. Magn. & Magn. Mat. (1980), 20, 201.

45. W.M. Saipallah, B.W. Kadir, C. Hayzelden and B. Cantor, "Epoxy Resin-Metallic Glass Composites", J. Mat. Sci. (1980) 15, 266.

46. E. Babić, R. Ristić, M. Miljać, G. Gregan and M.G. Scott, "Superconductivity in Zr-Ni Glasses", Solid State Comm., in press.

47. K. Hoselitz, "The Saturation Magnetization of Some Substituted Fe-Si-B Glasses", Phys. Stat. Sol. (a) 65 (1981) no. 1.

5. Some Fruits of the Sussex Researches

Since a Final Report only has space to outline the outcome of such extensive research, I shall merely highlight what I regard as the most important groups of findings:

(i) The work on martensite formation in rapidly quenched iron and iron alloys has been most successful; transformation temperatures, hysteresis, crystallographs, mechanisms and hardness have all come to be much bette. understood. The work on zirconium-base alloys performed during a most productive year by our Indian visitor, Dr. Banerjee, was also most informative.

Two very detailed papers (Inokuti and Cantor; Duflos and Cantor) are in press.

(ii) The work on relaxation and crystallization of metallic glasses has absorbed about 50% of our efforts. A very intensive study has been made of the Zr-Ni glasses, including, very recently, a study of neutron irradiation effects (examined calorimetrically and dilatometrically).

One major innovation, conceived after our proposal was submitted to O.N.R., was to use a novel instrument, with a precision better than one part in 1000, to measure Young's modulus of metallic glass tapes, and to use this to study relaxation, especially reversible features, in various glasses: this technique, introduced by A. Kuršumović and M.G. Scott, has proved very powerful.

The other major innovation was to make precise length change (and density) measurements, which has uncovered anomalies which are as yet unexplained.

(iii) The third area of major advance, at a very rapid pace in the last 2 years, has been in the study of diffusion in metallic glasses. Three techniques have been used to very good effect: secondary ion mass spectrometry, to profile boron; a nuclear reaction between energetic protons and boron nuclei, to profile boron; Rutherford

back-scattering of helium ions, to profile heavy atoms.

These 3 techniques have allowed us to measure the diffusivity of boron in a Ni-Nb glass over a much wider temperature range than in any other diffusion investigation (finding a non-Arrhenius temperature relationship); to show the existence of distinct interstitial and substitutional diffusion modes; to show how different heavy atoms (Au,Pt,Pb) diffuse in the same glass; to prove the absence - contrary to earlier reports - of effects of relaxation of a glass on diffusivities therein; to study the effect of irradiation on diffusivity in a glass.

Our results are being fully presented at the forthcoming RQ4 Conference in Japan.

6. Future Researches

We think that, in particular, there is a great deal more to be done on the following fronts:

(i) Relaxation of metallic glasses, studied by elastic modulus measurements and dilatometry.

(ii) Diffusion of different species in a single metallic glass, and effects of solute concentration in a glass on self-diffusion of that solute.

(iii) Generally, the effects of ultrasmall as-quenched grain size on various properties of rapidly quenched crystalline alloys, especially martensitic transformations and strength (critical study of the Petch relationship).

We also persist in our view of 4 years ago that there is much scope for systematic study of rapidly quenched age-hardening systems